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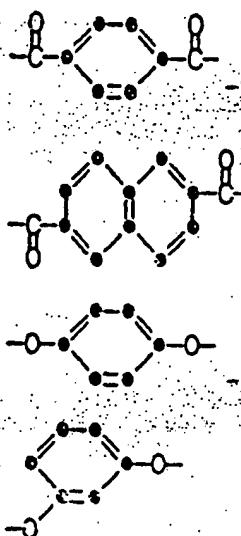
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification:  C08G 63/18	A1	(11) International Publication Number: WO 79/01040  (43) International Publication Date: 29 November 1979 (29.11.79)
(21) International Application Number: PCT/US79/00214		(74) Agent: KLINE, William, H. J.; Eastman Kodak Company, 343 State Street, Rochester, NY 14650 (US).
(22) International Filing Date: 5 April 1979 (05.04.79)		
(31) Priority Application Number: 903,437		(81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP.
(32) Priority Date: 8 May 1978 (08.05.78)		
(33) Priority Country: US		Published with: <i>International search report</i>
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(54) Title: LIQUID CRYSTAL COPOLYESTERS

## (57) Abstract

Liquid crystal copolymers having melting points low enough to allow the copolymers to be melt-processed in conventional equipment. The copolymers are prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol and contain the following divalent radicals:



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## LIQUID CRYSTAL COPOLYESTERS

### Technical Field

This invention relates to liquid crystal co-polyesters having the high mechanical properties of liquid crystal copolyesters and melting points low enough to allow the copolyesters to be melt-processed into useful articles using commercially available equipment.

### 10 Background of the Invention

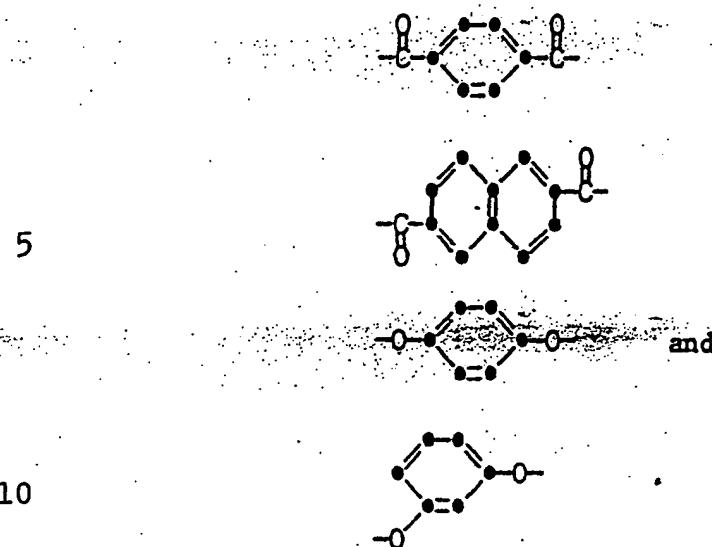
Liquid crystal copolyesters that are all-aromatic have excellent mechanical properties. Examples of these polyesters are the copolyesters prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, hydroquinone and resorcinol. U.S. Patents 3,160,602 and 3,778,410 describe processes that can be used to prepare these copolyesters. It has been difficult to use these copolyesters because the melting points of the polymers have been so high that the polymers cannot be melted and formed into useful articles in conventional processing equipment.

### Disclosure of Invention

We have found that certain all-aromatic co-polyesters prepared from terephthalic acid, 2,6-naphthalene dicarboxylic acid, hydroquinone and resorcinol have melting points that are low enough to permit the copolyesters to be processed into useful articles, such as fibers and molded articles, in conventional equipment.

The copolyesters of this invention are prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol and can be defined as copolyesters having molecular weights suitable for forming fibers and containing the following divalent radicals:

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In our copolymers the range of terephthalic acid is from 20 to 50 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined. Since the range of terephthalic acid is based on the sum of the moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid, at 20 mole percent terephthalic acid the copolymers have 80 mole percent 2,6-naphthalenedicarboxylic acid and at 50 mole percent terephthalic acid the copolymers have 50 mole percent 2,6-naphthalenedicarboxylic acid.

In preferred copolymers the range of terephthalic acid is from 30 to 45 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined.

Also in our copolymers the amount of resorcinol is from 20 to 65 mole percent, based on the total moles of hydroquinone and resorcinol combined. Thus, at 25 mole percent resorcinol, the copolymers have 75 mole percent hydroquinone, and at 65 mole percent resorcinol the copolymers have 35 mole percent hydroquinone.

In preferred copolymers the range of resorcinol is from 30 to 50 mole percent, based on the total moles of resorcinol and hydroquinone.

The precise manner in which the melting points of the copolyesters of the invention are unexpectedly lower than the melting points of similar copolyesters is illustrated in the Figure.

5        In the Figure the amount of terephthalic acid, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid, has been plotted on the abscissa. The temperature in degrees Centigrade has been plotted on the ordinate. Melting points have been  
10      plotted for copolyesters of the invention, containing a quantity of terephthalic acid in the range of 20 to 50 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid.  
15      Suitable curves have been drawn through the data points for copolyesters containing the same amount of resorcinol. For example, the lowermost curve drawn through the closed circular data points represents the melting points of copolyesters containing 40 mole percent resorcinol, based on the total moles of hydroquinone and  
20      resorcinol combined.

The data for the copolyesters of the invention were obtained by preparing each of the copolyesters using a process known in the art and then determining the melting points of each copolyester.

25      The copolyesters of the invention were prepared by an acidolysis procedure whereby terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol were reacted under an increasing temperature ranging up to  
30      340-380°C. and a decreasing pressure to form a high molecular weight polymer. As a specific example, the following procedure was used to prepare a copolyester from 40 mole percent terephthalic acid and 60 mole percent 2,6-naphthalenedicarboxylic acid, based on the  
35      moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined, and 60 mole percent hydroquinone and

40 mole percent resorcinol, based on the moles of hydroquinone and resorcinol combined.

A mixture of 33.2 g. (0.20 mole) terephthalic acid, 64.8 g. (0.30 mole) 2,6-naphthalenedicarboxylic acid, 38.8 g. (0.20 mole) resorcinol diacetate, and 66.6 g. (0.30 mole) hydroquinone dipropionate was placed in a 500-ml. flask equipped with a stirrer, short distillation column and an inlet for nitrogen. The flask was evacuated and purged three times with nitrogen and dried at 100-110°C. for 30 minutes at <0.3 mm. pressure before being immersed in a bath at 275°C. After the mixture was stirred for 30 minutes at 280°C., the temperature was raised to 300°C. for 30 minutes and then to 325°C. for 30 minutes. Finally the temperature was raised to 355°C. for 25 minutes and a vacuum of 0.5 mm. was applied. The polymerization was complete within 20 to 30 minutes. The tough, fibrous, opaque polymer obtained had a softening point of 332°C. and a melting point of 341°C. Fibers with tenacities >3 g./denier can be melt spun at 360°C. Heat-treated fibers had tenacities of 10 g./denier and higher.

The other copolymers containing different amounts of 2,6-naphthalenedicarboxylic acid, terephthalic acid, hydroquinone and resorcinol were prepared by a similar procedure but using slightly different reaction temperatures because of differences in melting points.

Solid-phase polymerization also may be used to increase the molecular weight of the copolymers of the invention by heating polymer particles in an inert atmosphere or under reduced pressure at a temperature below that at which the particles will become tacky and tend to fuse together. Since this thermal treatment may give polymers with increased crystallinity and melting points, compared to melt phase

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polymerization, melt phase polymerization is generally preferred. Solid-phase polymerization is preferred, however, if the melting point is above 380°C.

5 The melting points of the copolyesters of the invention were determined with a differential scanning calorimeter.

The accompanying Figure shows that the melting points of the copolyesters of the invention containing 20 to 50 mole percent terephthalic acid and 20 to 65 10 mole percent resorcinol are unexpectedly lower than the melting points of copolyesters containing less than 20 or more than 50 mole percent terephthalic acid. For example, consider the copolyester which contains a constant value of 40 mole percent resorcinol and is represented by the lower curve connecting the closed circular data points. When the amount of terephthalic acid is below 20 mole percent, the melting point is above 400°C. As the amount of terephthalic acid is increased, the melting point falls and reaches a minimum value of 20 330°C. at 30 mole percent terephthalic acid. As the amount of terephthalic acid is increased, the melting point increases and is 385°C. at 50 mole percent terephthalic acid.

Although the details of the reduction in melting point have been discussed only for the copolymers containing 40 mole percent resorcinol, the same lowering of the melting point applies to the other copolymers of this invention. For example, the melting point of the copolymers containing 20 and 60 mole percent resorcinol is also substantially lowered when from 30 20 to 50 mole percent terephthalic acid is used. Although melting point data is not plotted for copolymers containing less than 20 mole percent terephthalic acid, it is clear from the shape of the curve melting 35 points are above 400°C.

A wide variety of diacyl esters of hydroquinone and resorcinol can be used to prepare the copolyesters of this invention. Examples of diesters include the diacetate, dipropionate, dibutyrate and dibenzoate.

5 The diacetate and dipropionate are preferred.

The copolyesters of this invention can contain minor amounts of other naphthalenedicarboxylic acid isomers in addition to the 2,6-isomer. Also, minor amounts of dicarboxylic acids other than terephthalic

10 acid and diols other than hydroquinone can be used.

The copolyesters of this invention can also contain nucleating agents, fillers, pigments, glass fibers, asbestos fibers, antioxidants, stabilizers, plasticizers, lubricants, fire-retardants, and other additives.

15 The inherent viscosity of the copolyesters of this invention cannot be determined because the copolyesters of this invention are insoluble in typical solvents used for determining inherent viscosity. Although the inherent viscosity of the copolyesters of the invention has not been measured, the molecular weights of the copolyesters of the invention are high enough to be in the fiber-forming range. The minimum fiber-forming molecular weight of the copolyesters is about 5,000. In most cases copolyesters of the invention have molecular weights above 8,000 and can have molecular weights as high as 20,000 and in some instances the molecular weights can range up to 25,000 or even higher.

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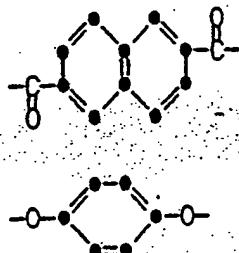
We Claim:

1. Copolyesters having a fiber-forming molecular weight and containing the following divalent radicals:

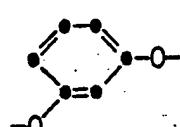
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the copolyesters being characterized by the amount of



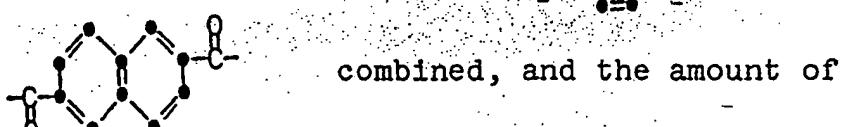
being from 20 to 50 mole percent,

20

based on the total moles of



and



combined, and the amount of

25

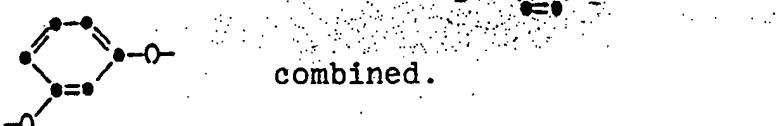
being from 20 to 65 mole percent,

30

based on the total moles of



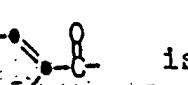
and



combined.

2. The copolyester of Claim 1 wherein the

range of the amount of

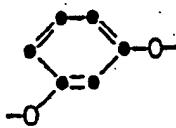


is from 30 to

35

45 mole percent and the range of the amount of

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is from 30 to 50 mole percent.

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## INTERNATIONAL SEARCH REPORT

79101040

International Application No PCT/US79/00214

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

INT.CL. C08G 63/18;  
U.S. CL. 528/190

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>14</sup>

Classification System	Classification Symbols
US	528/190; 528/193; 528/194

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>15</sup>

III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>16</sup>

Category <sup>17</sup>	Citation of Document, <sup>18</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US, A, 3,160,602, PUBLISHED 08 DECEMBER 1964, KANTOR ET AL.	1-2
X	US,A, 3,778,410, PUBLISHED 11 DECEMBER 1973 KUHFUSS ET AL.	1-2
A	US, A, 4,066,620, PUBLISHED 03 JANUARY 1978 KLEINSCHUSTER ET AL.	1-2
X,P	US, A, 4,118,372, PUBLISHED 03 OCTOBER 1978 SCHAEGEN	1-2
X,E	US,A, 4,156,070, PUBLISHED 22 MAY 1979 JACKSON, JR., ET AL.	1-2
X,E	US,A, 4153,779, PUBLISHED 08 MAY 1979 JACKSON, JR. ET AL.	1-2

\* Special categories of cited documents:<sup>16</sup>

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

## IV. CERTIFICATION

Date of the Actual Completion of the International Search<sup>19</sup>

07 AUGUST 1979

Date of Mailing of this International Search Report<sup>20</sup>

13 AUG 1979

International Searching Authority<sup>21</sup>

ISA/US

Signature of Authorized Officer<sup>20</sup>

LESTER L. LEE

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